CRC Handbook of Biosolar Resources

Editor-in-Chief

Oskar R. Zaborsky
National Science Foundation
Washington, D.C.

Volume II

Resource Materials

Editors

Thomas A. McClure
Senior Economist
Battelle Columbus Laboratories
Columbus, Ohio

Edward S. Lipinsky
Senior Research Leader
Battelle Columbus Laboratories
Columbus, Ohio

CRC Press, Inc.
Boca Raton, Florida

BOTANOCHEMICAL CROPS

R. A. Buchanan and James A. Duke

TRADITIONAL BOTANOCHEMICALS

Green plants produce an array of substances that can substitute for, or complement, the use of petroleum-derived products. These substances are now generally called botanochemicals (a term coined by the U.S. Department of Agriculture public information officer, Mr. Dean Mayberry), analogous to petrochemicals.* Botanochemicals include such traditional products as those listed in Table 1. Although one author (James Duke) suggests that U.S. dependence on imported essential oils, specialty plant fibers, and vegetable dyestuffs could be greatly reduced by employing integrated production schemes of the type envisioned for new multiuse botanochemical crops, the term "botanochemical" has not been generally construed to include these classes of plant-derived materials. Furfural differs from other products in Table 1 in that it represents a derived or secondary botanochemical, not produced directly by the green plant itself but manufactured in quantity from plant materials. Other examples of important or potentially important secondary botanochemicals include such fermentation products as acetone, butanol, ethanol, glycols, and methane. Traditional botanochemicals are important items of commerce, but their consumption has been small in comparison to total petrochemical consumption. However, now that the price of petrochemicals is increasing relatively faster than the price of agricultural products, the latter are increasingly attractive as industrial feedstocks. Several of the botanochemicals of Table 1 are by-products from the production and processing of plants for other major uses; thus, even the sources of these traditional botanochemicals may be considered as multiuse crops.

Table 1 also indicates U.S. dependence annually on more than $1 billion worth of imported botanochemicals. It is possible that in the future these products could be produced by U.S. agriculture.

NEW SPECIALTY OILSEED CROPS

An active program of new crops research has been conducted for almost 20 years with the aim of developing potential new crops for the production of seed oils with special characteristics for industrial (nonfood) uses.[1] Some more promising candidates for new industrial oilseed crops are presented in Table 2, and an estimate of the currently needed production is given in Table 3.[1] The value and need for such products increases as the price of petroleum rises. An important factor in the production economics of industrial seed oils is the utilization of their generally high-protein oilseed meal by-product.

POTENTIAL NEW MULTIUSE CROPS

Plant Extractives and Their Fractionation

Many presently unutilized plant species contain, on a dry weight basis, up to about

* Nomenclature for plant species is after (1) L. H. Bailey Hortorium Staff, *Hortus Third*, Macmillan, New York, 1976, 1290 pp.; (2) Terrell, E. E., A Checklist of Names for 3,000 Vascular Plants of Economic Importance, *U.S. Dep. Agric. Agric. Handb.*, No. 505, 1977, 201 pp.; and (3) *Index Kewensis* (and supplements), Jackson, B. D. et al., Oxford University Press, Oxford, 1885 to 1973.

Table 1
THE U.S. MARKET FOR TRADITIONAL BOTANOCHEMICALS

Product	U.S. industrial source	Important plant species	Annual U.S. consumption: Quantity, million kg	Annual U.S. consumption: Year	Current unit value,[a] \$/kg
Crude tall oil[b]	Kraft paper pulping	*Pinus* sp.	514	1977	0.17
Naval stores[b]	Gum and wood distillation	*Pinus elliottii, P. palustris*			
Turpentine			18.1	1974	0.50
Rosin			141	1974	0.62
Vegetable oils[c]	Oilseed processing	*Glycine max, Elaeis guineensis*	551.5	1977	0.54[c]
Natural waxes[d]	Imported	*Copernicia prunifera, Euphorbia antisyphilitica*	5.2	1976	3.00[d]
Vegetable tanning materials[e]	Imported	*Acacia* sp., *Schinopsis* sp., and others	30.6	1977	0.36[e]
Furfural	Acid hydrolysis of agricultural residues	*Avena sativa, Zea mays*	90.7[f]	1978	1.14
Natural rubber	Imported	*Hevea brasiliensis*	775	1978	1.34
Gutta (balata, gutta percha, pontianak, jelutong)	Imported	*Manilkara bidentata, Palaquium gutta*	2.4	1977	2.22[a]

[a] December 1978 prices except for tanning materials,[e] and for gutta, for which average 1977 price of several grades is given.

[b] Naval stores usually include tall oil products. In order to avoid overlapping, quantities here are for consumption of crude tall oil in selected products and for the total production of the gum and wood distillation industries, respectively.

[c] Vegetable oils for nonfood industrial uses include a considerable quantity of such expensive specialty products as tung and castor oils. Price here is for crude soya oil.

[d] The price range for the various imported waxes is large; the price given is for carnauba wax.

[e] Consumption of vegetable tannins has been continuously decreasing since about 1950. Quantity is the total amount of imported materials, not adjusted for actual tannin content. The largest volume imports are processed chestnut (*Castanea*), hemlock, (*Tsuga*), and divi-divi (*Caesalpinia*), quebracho (*Schinoposis*) extract, and wattle (*Acacia*) extract. Price is total 1977 import value divided by total quantity.

[f] Estimated domestic market.

Table 2
POTENTIAL NEW CROP SOURCES OF INDUSTRIAL OILS[1]

Species	Component in triglyceride oil
Species with long-chain fatty acids in seed oil[a]	
Crambe abyssinica	C_{22} (60%)
Lunaria annua	C_{22} (20%), C_{24} (40%)
Limnanthes alba	C_{22} + C_{20} (95%)
Selenia grandis	C_{22} (58%)
Leavenworthia alabamica	C_{22} (50%)
Marshallia caespitosa	C_{22} (44%)

Table 2 (continued)
POTENTIAL NEW CROP SOURCES OF INDUSTRIAL OILS[1]

Species with hydroxy and keto fatty acids[b]

Lesquerella gracilis	14-OH-C_{20} (70%)
Holarrhena antidysenterica (?)	9-OH-C_{18} (70%)
Cardamine impatiens	Dihydroxy C_{22} and C_{24} (23%)
Chamaepeuce afra	Trihydroxy C_{18} (35%)
Lesquerella densipila	12-OH-C_{18} diene (50%)
Dimorphotheca sinuata	9-OH-C_{18} conj. diene (67%)
Coriaria myrtifolia	13-OH-C_{18} conj. diene (65%)
Cuspidaria trifoliata	Keto acids (25%)

Potential sources of epoxy fatty acids[c]

Species	Component in triglyceride oil
Vernonia anthelmintica	68—75%
Euphorbia lagascae	60—70
Stokesia laevis	75
Cephalocroton pueschelii	67
Erlangea tomentosa	50
Alchornea cordifolia	50 (C_{20})
Schlectendalia luzulaefolia	45

Sources of conjugated unsaturation[d]

Valeriana officinalis	40% 9; 11, 13
Calendula officinalis	55% 8, 10, 12
Centranthus macrosiphon	65% 9, 11, 13
Impatiens edgeworthii	60% 9, 11, 13, 15
Dimorphotheca sinuata	60% 10, 12 (+ hydroxy)
Coriaria myrtifolia	65% 9, 11 (+ hydroxy)

Source of liquid wax esters[e]

Simmondsia chinensis	30% C_{40}, 50% C_{42}

[a] Percentage and chain length of major fatty acid as number of carbon atoms given.
[b] Type and location of functional groups, chain length, and percentage of major fatty acids given.
[c] Percentage of epoxy fatty acid given.
[d] Location of conjugated unsaturation and percentage of unsaturated fatty acid indicated.
[e] Percentage and chain length of aliphatic wax esters given.

Table 3
CURRENTLY NEEDED PRODUCTION OF SELECT NEW TYPES OF INDUSTRIAL OILS[1]

Crop species	Common name	Oil type	Needed production (million kg)	Yield (kg/ha)	Crop area (1000 ha)
Crambe abyssinica	Crambe	Long-chain fatty acids	13.6	1121	12.1
Simmondsia chinensis	Jojoba	Liquid wax esters	45.4	2242	20.2
Lesquerella gracilis	Lesquerella	Hydroxy fatty acids	90.7	1121	80.9
Stokesia laevis	Stokes' aster	Epoxy fatty acid	136.1	1121	121.4

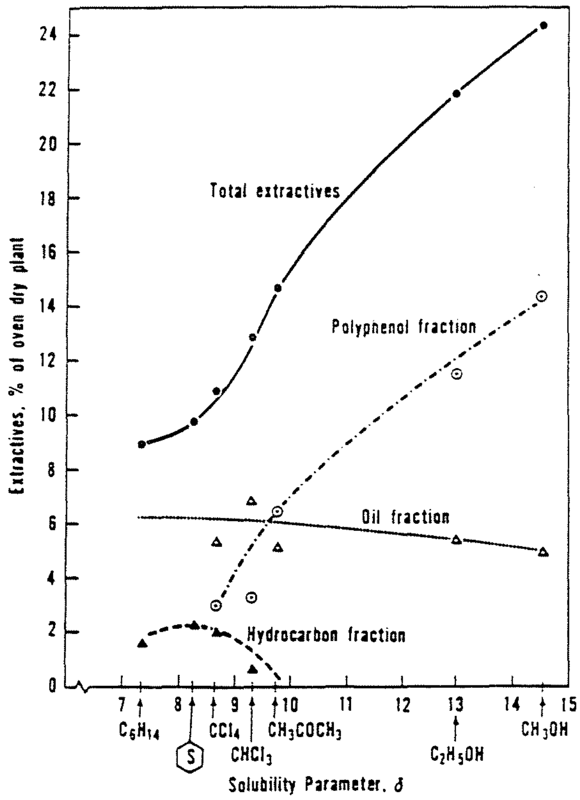

FIGURE 1. Exhaustive Soxhlet extraction of common milkweed (*Asclepias syriaca*) with various organic solvents.

30% of organic soluble extractives and are potentially nontraditional sources of botanochemicals. Several of these species contain more than 5% "whole-plant oil", either as the major component of a latex (milky sap) or else otherwise distributed throughout major plant tissues. Whole-plant oils differ from conventional vegetable oils in that they are not concentrated in storage organs (seeds or fruits), and they are much more complex in composition. Although there has been little past interest in processing whole plants for oils, there is now general recognition that they are potentially very important new and renewable sources of raw materials and energy. However, an economic requirement for processing whole plants is that markets be developed for each plant product, including low unit-value fibrous residues. Thus, such botanochemical crops would actually be multiuse crops and would provide fiber, carbohydrate, and protein as well. Alternative products may include drug intermediates, dyes, essential oils, flavoring materials, and specialty fibers. Botanochemical crops would lead to a more adaptive agriculture whose products varied with changing market and even social needs.[2] A scenario has been developed for their introduction into U.S. agriculture.[3] Most of the data in subsequent tables are taken from the scenario.[3]

The quantity and composition of extractives from a given plant depend on solvent and method of extraction as illustrated by exhaustive Soxhlet extraction of common milkweed (Figure 1). Solvents with a solubility parameter (δ) above 9.7 extract a broad range of complex substances but do not extract polymeric hydrocarbons and hard waxes. Solvents with δ below about 8.2 extract little of the more polar components ("polyphenol fraction"), but do extract hydrocarbon polymers ("hydrocarbon fraction"). Any of the organic solvents extract all or nearly all of the nonpolymeric neutral lipids, designated "oil-fractions" or "whole-plant oils."

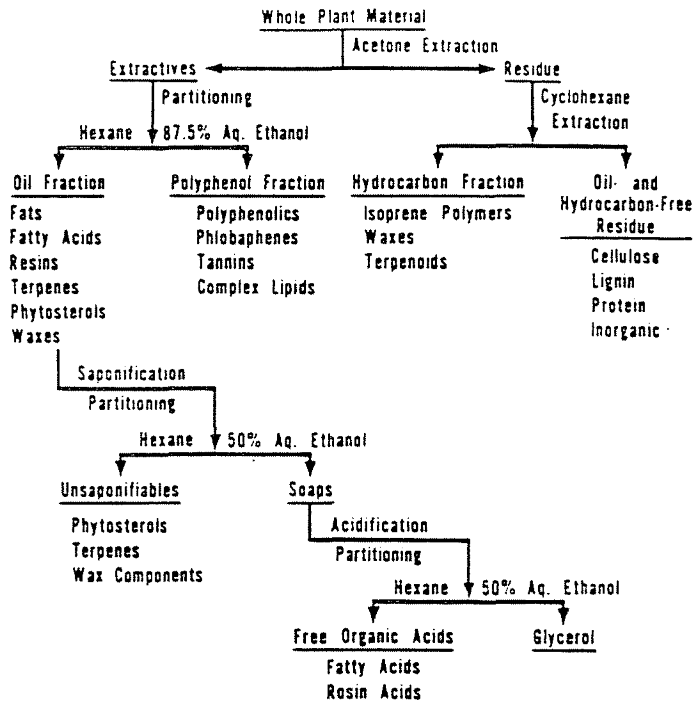

FIGURE 2. Scheme for extracting and partitioning whole-plant samples in laboratory preparation of botanochemicals.

As can be deduced from Figure 1, several alternative extraction-partitioning schemes can be employed to characterize plant extractives. The modification of the classic sequential acetone-benzene extraction scheme shown in Figure 2 was used to obtain data presented in subsequent tables. The quality of separations achieved in partitioning plant materials by this method is indicated by carbon-hydrogen values for representative fractions in Table 4. Heating values, estimated by Kronberger's concept of organic oxidation,[4] are included to allow rough energy calculations from the data in subsequent tables.

Promising Species

Botanical characteristics of several promising species are given in Table 5. In general, it is desirable that botanochemical crops be perennials which rapidly grow back from their rootstocks when cut off at ground level. Woody species (*Sassafras albidum, or Lonicera tatarica*, for example) could be handled as short-rotation forestry crops. Herbaceous species (*Asclepias syriaca, Solidago* sp., for example) could be handled like alfalfa to provide more than one harvest per growing season.

Composition of representative plants from promising species are given in Table 6. In Table 6, polyphenol, oil, and polymeric hydrocarbon fractions are defined by the method of preparation illustrated in Figure 2. For a few additional (mainly far-western U.S.) species, a more detailed analysis obtained by a similar extraction procedure followed by nuclear magnetic resonance (NMR) estimation of compound distributions is given in Table 7.[5] Fiber properties for a few species evaluated as having good crop potential for botanochemicals are included in Table 8.[6] All the plants except *Cirsium discolor, Phytolacca americana*, and *Solidago graminifolia* in Table 8 were rated as offering potential for paper pulping.[6] Paper pulping is compatible with botanochemical recovery and could lead to novel "tall-oil products" if practiced with these plants.

Table 4
FRACTIONATION OF PLANT MATERIALS, QUALITY OF SEPARATION,[a] AND ESTIMATED HEATING VALUE FOR COMPONENTS

Plant fraction	Carbon values range (%)	Hydrogen values range (%)	Estimated heating value (MJ/kg)[b]
Whole plant			
Analytical values, 2 samples	43.6—48.5	6.2—6.6	17.2
Polyphenol fraction			
Analytical values, 3 samples	52.1—57.0	6.7—7.7	20.8
Standard, quercetin, ($C_{15}H_{10}O_7$)	59.60	3.38	
Oil fraction			
Analytical values, 7 samples	75.6—79.7	10.8—11.4	39.5
Standard, triolein $C_{57}H_{104}O_6$)	77.30	11.85	
Hydrocarbon fraction			
Analytical values, 4 samples	79.9—88.1	11.0—12.6	46.1
Standard, cetyl stearate, ($C_{34}H_{68}O_2$)	80.24	13.47	
Standard, polyisoprenes [($C_5H_8)_n$]	88.16	11.84	

[a] Samples from several different plant species were analyzed, and the range of values is given in comparison with calculated values for standard materials.

[b] Heating value estimated for plant fractions of median C and H content using Kronberger's concept.[4]

Productivity Estimates

Few estimates have been given for productivity of the potential new multiuse botanochemical crops to be developed by domestication of wild species. Table 9 compares yields and products from unimproved wild milkweed (*Asclepias syriaca*) with estimated yields from an improved crop variety. Overall, Table 9 estimates an increase in total botanochemical production from 1824 kg/ha to 4484 kg/ha. A large portion of this increase can probably be achieved simply by harvesting leafier plants (not allowing seed to develop and mature leaves to drop) by clipping more than once during the growing season, as is done with forage crops. In milkweed, as in many other plants, leaves are much richer in extractives than stems.

Models have been developed for each of four potential types of botanochemical crops, and their yields have been estimated (Table 10).

New Botanochemical Products

Whole Plant Oils

An estimation, based on thin-layer chromatography, of the relative amounts of the lipid classes present in whole plant oils is given in Table 11 for 14 productive plant species. Note that results for *Euphorbia lathyris* in Table 11 are not consistent with those in Table 7, particularly for triglycerides in leaves and stems. Neither method of estimation is very satisfactory, and detailed quantitative analyses are badly needed.

Results have also been reported from examination of the latices for a few species (Table 12).[5]

Whole-plant oils are mainly of interest as industrial raw materials. Depending on species chosen for crop production and the processing technology employed, a wide variety of chemical intermediates could be produced, including sterols, long-chain alcohols, rosin and fatty acids, esters, waxes, terpenes, and other hydrocarbons. A substantial market probably exists for crude or slightly refined oils rich in nonglyceride

Table 5
BOTANICAL CHARACTERISTICS OF SEVERAL POTENTIAL, MULTI-USE BOTANOCHEMICAL CROPS[a]

		Growth characteristics			Ecological characteristics	
Family-genus-species	**Common name**	**Life cycle and habit**	**Growth rate (m/yr)[b]**	**Adaptable to clipping[c]**	**Edaphic and climatic adaptation**	**Geographic (U.S.) distribution**
Aceraceae						
Acer saccharinum	Silver maple	Perennial, large tree, deciduous	3	Yes	Mesophyte, temperate	Maine, Fla., west to Minn., Okla.
Anacardiaceae						
Rhus glabra	Smooth sumac	Perennial, glabrous shrub or tree	2	Yes	Mesophyte, temperate	Eastern North America
Asclepiadaceae						
Asclepias hirtella	Green milkweed	Perennial, herbaceous	1	Yes	Mesophyte, temperate	Mich., Minn., south to Ala., Okla.
A. incarnata	Swamp milkweed	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Maine, Fla., west to Utah
A. subulata	Desert milkweed	Perennial, *Ephedra*-like undershrubs	1.5	Yes	Xerophyte, tropical	Calif., Ariz., Nev.
A. syriaca	Common milkweed	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Maine, S.D., south to Ga., Okla.
Cryptostegia grandiflora	Madagascar rubber vine	Perennial, woody evergreen vine	4	Yes	Mesophyte, tropical	Southern Fla., Puerto Rico
Caprifoliaceae						
Lonicera tatarica	Red tartarian honeysuckle	Perennial, deciduous shrub	2	Yes	Mesophyte	Widespread as cultivar escape
Sambucus canadensis	Common elder	Perennial, deciduous shrub	1.5	Yes	Mesophyte	Maine, Fla., and Tex.
Symphoricarpos orbiculatus	Coral berry	Perennial, deciduous shrub	1.5	Yes	Mesophyte, temperate	N.Y., Colo., south to Fla. and Tex.

Table 5 (continued)
BOTANICAL CHARACTERISTICS OF SEVERAL POTENTIAL, MULTI-USE BOTANOCHEMICAL CROPS[a]

		Growth characteristics			Ecological characteristics	
Family-genus-species	Common name	Life cycle and habit	Growth rate (m/yr)[b]	Adaptable to clipping[c]	Edaphic and climatic adaptation	Geographic (U.S.) distribution
Campanulaceae						
Campanula americana	Tall bellflower	Annual, herbaceous	1.5	Probably	Mesophyte, temperate	Eastern North America
Compositae						
Ambrosia trifida	Giant ragweed	Annual, herbaceous	2.5	Yes	Mesophyte, temperate	Entire U.S.
Cacalia atriplicifolia	Pale Indian-plantain	Perennial, herbaceous	2	Probably	Mesophyte, temperate	N.J., New England, south to Ga., Okla.
Chrysothamnus nauseosus	Rabbitbrush	Perennial, deciduous shrub	2	Probably	Xerophyte, temperate	Mont. to Tex., Calif.,
Cirsium discolor	Field thistle	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Minn. south to Va., Tenn., Mo., Kan.
Eupatorium altissimum	Tall boneset	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Penn., New England, south to Ala., Tex.
Helianthus grosseserratus	Large-toothed sunflower	Perennial, herbaceous	3	Yes	Mesophyte, temperate	N.Y. to Tex.
Parthenium argentatum	Guayule	Perennial, woody shrub	1	Yes	Xerophyte, warm temperate	Tex., N.M.
Rudbeckia subtometosa	Sweet coneflower	Perennial, herbaceous	1.5	Probably	Mesophyte, temperate	Wis. south to Tex., La.
Silphium integrifolium	Rosinweed	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Ohio, Minn., south to Miss., Okla.,
S. laciniatum	Compass plant	Perennial, herbaceous	2	Yes	Mesophyte, temperate	Ohio, S.D., south to Ala.,Tex.
S. terebinthinaceum	Prairie dock	Perennial, herbaceous	2	Yes	Mesophyte, temperate	Ohio, Minn. to Ga., La.,
Solidago graminifolia	Grass-leaved goldenrod	Perennial, herbaceous	1	Yes	Mesophyte, temperate	Maine, Md., west to Minn., Mo.

Table 5 (continued)
BOTANICAL CHARACTERISTICS OF SEVERAL POTENTIAL, MULTI-USE BOTANOCHEMICAL CROPS[a]

		Growth characteristics			Ecological characteristics	
Family-genus-species	Common name	Life cycle and habit	Growth rate (m/yr)[b]	Adaptable to clipping[c]	Edaphic and climatic adaptation	Geographic (U.S.) distribution
Compositae (cont.)						
S. leavenworthii	Edison's goldenrod	Perennial, herbaceous	3	Yes	Mesophyte, warm temperate	Southeastern U.S.
S. rigida	Stiff goldenrod	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Mass. to Tex.
Sonchus arvensis	Sow thistle	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Eastern U.S.
Verbesina alternifolia	Wing-stem	Perennial, herbaceous	1.5	Probably	Mesophyte, temperate	N.Y. Ill., Iowa, south to La., Okla.
Vernonia altissima	Tall ironweed	Perennial, herbaceous	2	Yes	Mesophyte, temperate	Western N.Y., Mo., to Ga., La.
V. fasciculata	Ironweed	Perennial, herbaceous	1.5	Yes	Mesophyte, temperate	Ohio, Minn. south to Mo., Okla.
Eleagnaceae						
Elaeagnus multiflora	Cherry elaeagnus	Perennial, deciduous shrub	2	Yes	Mesophyte	Widespread (as cultivar)
Ericaceae						
Xylococcus bicolor	Manzanita	Perennial, evergreen arborescent shrub	2.5	Yes	Xerophyte	Calif.
Euphoribiaceae						
Euphorbia dentata	Cut-leaf spurge	Annual, herbaceous	0.5	Doubtful	Mesophyte, temperate	N.Y., Wyo. south to Tex.
E. lathyris	Mole plant	Annual or biennual, herbaceous	1	Probably	Mesophyte, temperate	Conn. to Va., southwestern U.S.
E. pulcherrima	Poinsettia	Perennial, evergreen, herbaceous	3	Yes	Mesophyte, tropical	Fla. subtropical southwestern U.S.

Table 5 (continued)
BOTANICAL CHARACTERISTICS OF SEVERAL POTENTIAL, MULTI-USE BOTANOCHEMICAL CROPS[a]

		Growth characteristics			Ecological characteristics	
Family-genus-species	Common name	Life cycle and habit	Growth rate (m/yr)[b]	Adaptable to clipping[c]	Edaphic and climatic adaptation	Geographic (U.S.) distribution
Gramineae						
Agropyron repens	Quackgrass	Perennial grass	1	Yes	Mesophyte, temperate	Northern U.S. south to N.C., Calif.
Elymus canadensis	Canada wildrye	Perennial grass	1.5	Yes	Mesophyte,	Northern U.S. south to N.C., Calif.
Phalaris canariensis	Canarygrass	Annual grass	1	Yes	Mesophyte, temperate	Nearly entire U.S.
Labiatae						
Pycnanthemum incanum	Mountain mint	Perennial, herbaceous	1	Yes	Mesophyte, temperate	Vt., Ill. south to N.C., Tenn.
Teucrium canadense	American germander	Perennial, herbaceous	1	Yes	Mesophyte, temperate	Eastern North America
Lauraceae						
Sassafras albidum	Sassafras	Perennial, large deciduous tree	3	Yes	Mesophyte, temperate	Maine, Fla. to Tex.
Phytolaccaceae						
Phytolacca americana	Pokeweed	Perennial, herbacious	2.5	Yes	Mesophyte, temperate	Maine, Fla. west to N.M.
Rhamnaceae						
Ceanothus americanus	New Jersey tea	Perennial, deciduous shrub	1.5	Yes	Mesophyte	Maine to S.C., west to Tex.
Rosaceae						
Prunus americana	Wild plum	Perennial, deciduous tree	3	Yes	Mesophyte	Ind., Del. south to Tenn., Tex.

[a] List prepared January 1979; there is an on-going screening program for identification of promising species.
[b] For evergreen and woody perennials, this is the estimated height attained in a single growing season following clipping (pollarding) to near ground level. For annuals and herbaceous perennials, it is the usual mature height of the plants.
[c] Plants known to grow back vigorously from the root stock when clipped at near ground level are considered adaptable to clipping.

Table 6
COMPOSITION OF REPRESENTATIVE PLANTS FROM BOTANOCHEMICAL-PRODUCING SPECIES

		Typical composition of wild plants						
							Polymeric hydrocarbons	
Family—genus—species	Common name	Ash (%)	Crude protein (%)	Polyphenol fraction (%)		Oil fraction (%)	(%)	Type
Aceraceae								
Acer saccharinum	Silver maple	2.8	15.8	19.2		2.29	0.38	
Anacardiaceae								
Rhus glabra	Smooth sumac	6.9	6.6	18.8		5.51	0.20	Wax
Asclepiadiaceae								
Asclepias hirtella	Green milkweed	8.6	13.0	4.0		7.07	0.45	NR
A. incarnata	Swamp milkweed	9.8	9.9	10.4		[illegible]	[illegible]	[illegible]
A. subulata	Desert milkweed				11.4		[illegible]	[illegible]
A. syriaca	Common milkweed	9.9	11.1	7.2		4.29	[illegible]	[illegible]
Cryptostegia grandiflora	Madagascar rubber vine				6.7		2.19	NR
Caprifoliaceae								
Lonicera tatarica	Red tararian honeysuckle	7.5	9.4	14.6		3.15	1.64	NR
Sambucus canadensis	Common elder	4.5	6.2	6.3		2.13	0.50	NR
Symphoricarpos orbiculatus	Coral berry	4.5	5.6	10.6		2.19	0.77	NR
Campanulaceae								
Campanula americana	Tall bellflower	6.2	9.1	5.8		6.07	0.93	NR & wax

Table 6 (continued)
COMPOSITION OF REPRESENTATIVE PLANTS FROM BOTANOCHEMICAL-PRODUCING SPECIES

		Typical composition of wild plants						
							Polymeric hydrocarbons	
Family—genus—species	Common name	Ash (%)	Crude protein (%)	Polyphenol fraction (%)		Oil fraction (%)	(%)	Type
Compositae								
Ambrosia trifida	Giant ragweed	8.0	10.5	4.1		7.60	0.55	NR
Cacalia atriplicifolia	Pale Indian-plantain	9.4	10.6	8.5		3.06	3.10	NR
Chrysothamnus nauseosus	Rabbitbrush				—11.5—		1.67	NR
Cirsium discolor	Field thistle	9.7	5.3	3.5		5.24	0.36	NR & wax
Eupatorium altissimum	Tall boneset	6.5	8.0	10.1		5.52	0.52	NR & wax
Helianthus grosseserratus	Cut-leaf sunflower	9.8	7.9	8.3		2.06	0.69	NR
Parthenium argentatum	Guayule	8.1	16.6	7.1		4.04	4.58	NR
Rudbeckia subtomentosa	Sweet coneflower	—	5.9	7.8		2.37	1.22	NR
Silphium integrifolium	Rosin weed	11.0	5.5	6.2		2.52	0.70	NR
Silphium laciniatum	Compass plant	9.0	8.9	7.4		3.00	0.68	NR
S. terbinthinaceum	Prairie dock	9.7	4.1	5.7		2.49	0.85	NR
Solidago graminifolia	Grass-leaved goldenrod	5.4	5.3	12.7		2.47	1.43	NR
S. leavenworthii	Edison's goldenrod	10.2	11.6	8.0		4.48	1.37	NR
S. rigida	Stiff goldenrod	6.0	4.6	6.4		2.21	1.39	NR
Sonchus arvensis	Sow thistle		9.3	11.0		5.32	0.72	NR & wax
Verbesina alternifolia	Wing-stem	—	10.4	3.0		2.14	0.78	NR
Vernonia altissima	Tall ironweed	14.5	18.5	5.9		2.62	0.33	
V. fasciculata	Ironweed	7.9	10.5	7.7		5.01	0.36	NR
Elaeagnaceae								
Elaeagnus multiflora	Cherry elaeagnus	8.1	10.9	17.4		2.08	1.87	NR

Table 6 (continued)
COMPOSITION OF REPRESENTATIVE PLANTS FROM BOTANOCHEMICAL-PRODUCING SPECIES

		Typical composition of wild plants					
						Polymeric hydrocarbons	
Family—genus—species	Common name	Ash (%)	Crude protein (%)	Polyphenol fraction (%)	Oil fraction (%)	(%)	Type
Ericaceae							
Xylococcus bicolor	Manzanita	3.7	6.9	17.9	5.18	1.04	NR
Euphorbiaceae							
Euphorbia dentata	Cut-leaf spurge	13.8	16.7	3.5	9.68	0.17	
E. lathyris	Mole plant	7.3	11.8	7.1	9.21	0.37	
E. pulcherrima	Poinsettia	9.3	14.9	5.8	5.74	0.60	Wax
Gramineae							
Agropyron repens	Quackgrass	11.8	10.8	4.1	2.08	1.72	Gutta
Elymus canadensis	Canada wildrye	5.3	6.6	5.2	1.64	1.28	Gutta
Phalaris canariensis	Canarygrass	11.8	8.4	4.9	2.05	1.15	Gutta
Labiatae							
Pycnanthemum incanum	Mountain mint	9.0	12.1	7.3	2.02	1.24	NR
Teucrium canadensis	American germander	8.2	13.1	15.3	2.51	1.32	NR
Lauraceae							
Sassafras albidum	Sassafras	3.4	8.6	13.9	5.55	0.22	Wax
Phytolaccaceae							
Phytolacca americana	Pokeweed		15.5	5.9	3.41	0.17	
Rhamnaceae							
Ceanothus americanus	New Jersey tea	4.9	11.8	12.2	3.27	0.64	Wax
Rosaceae							
Prunus americanus	Wild plum	14.6	14.8	15.8	3.93	0.17	

Table 7
ESTIMATED COMPOSITION OF EXTRACTIVES FROM VARIOUS PLANTS[a]

	Benzene extract			Acetone extract			
Plant	Rubber	Wax	Total	Glycerides	Isoprenoids	Other (terpenoids)	Total
Asclepias curassavica	0.6	<0.1	0.7	3.0	<0.5	2.0	5.9
Cryptostegia grandiflora	0.2	0.05	0.35	7.0	<0.5	6.0	13.3
Eucalyptus globulus	<0.01	0.05	0.1	3.5	<0.5	7.0	12.0
Euphorbia lathyris (leaves)	0.1	0.2	0.3	13.7	2.2	8.3	25.0
E. lathyris (seeds)				40.0	<0.1	<2.0	40.0
E. lathyris (stem)				1.9	<0.5	2.0	4.5
E. monteiroi	0.2	0.4	0.6	5.1	<0.5	3.3	9.5
E. tirucalli (UCB)[b]	0.07	0.13	0.2	2.4	<0.5	2.0	5.0
E. tirucalli (UCLA)[c]	0.1	0.3	0.4	4.4	<0.5	3.4	8.5
Hevea brasiliensis	1.3	0.2	1.5	5.1	<0.5	2.6	9.6
Jatropha curcas	<0.1	0.6	0.7	1.5	0.8	1.4	4.2
Monadenium rhizophorum	1.2	0.2	1.4	9.0	<0.5	6.0	16.5
Pedilanthus sp.	<0.1	<0.1	0.5	4.7	<0.5	2.3	8.7
Sarcostemma viminale	<0.1	0.8	0.8	6.6	<0.5	4.8	12.3
Synadenium grantii	0.4	0.4	0.8	6.6	<1.5	5.7	15.0

[a] Data are given in percent of plant dry weight. The plants (obtained from the collection of the Botany Department at the University of California, Davis) were dried in air, finely ground in a mortar, and extracted in a Soxhlet apparatus first for 8 hr with acetone and then for 8 hr with benzene. The solvents were evaporated, and the residue was taken up in $CDCl_3$. The compound distributions were estimated on the basis of 60-Mhz nuclear magnetic resonance spectra.[5]

[b] University of California, Berkeley.

[c] University of California, Los Angeles.

From Nielson, P. E. et al., *Science*, 198, 942, 1977.

Table 8
POTENTIAL OF SELECTED BOTANOCHEMICAL-PRODUCING SPECIES FOR PAPERMAKING[a]

Family-genus-species	Common name	Extractives (%)		Fiber content (%)			Average fiber length (mm)		
		Alcohol-benzene	1% NaOH	Maceration yield	M.E.A. cellulose[b]	α-Cellulose	Bast fiber	Woody fiber	Combined fiber
Asclepiadaceae									
Asclepias incarnata	Swamp milkweed	11.2	38.6	57.8	44.5	29.9	11.0	0.31	0.81
A. syriaca	Common milkweed	8.2	39.4	43.1	46.1	31.2	10.7	0.48	1.31
Caprifoliaceae									
Sambucus canadensis	Common elder	9.5	31.5	59.4	45.9	28.3	0.61	0.73	0.72
Compositae									
Ambrosia trifida	Giant ragweed	3.4	32.9	56.4	48.9	30.9	1.31	0.41	0.61
Cirsium discolor	Field thistle	7.5	44.7	45.7	42.1	27.2	0.90	0.63	0.70
Helianthus grosseserratus	Cut-leaf sunflower	6.5	39.2	53.2	46.2	29.4	1.14	0.74	0.83
Silphium integrifolium	Rosin weed	8.3	39.3	53.5	43.3	27.0	1.44	0.53	0.75
S. lacinatum	Compass plant	10.1	45.6	49.4	39.7	25.1	1.66	0.66	1.12
Solidago graminifolia	Grass-leaved goldenrod	7.0	34.0	40.3	38.2	20.6	[c]	0.31	0.31
Gramineae									
Elymus canadensis	Canada wildrye	15.2	51.2	39.6	42.9	27.0	[d]	[d]	1.00
Phytolaccaceae									
Phytolacca americana	Pokeweed	11.0	47.9	42.1	42.4	28.4	1.40	0.66	0.78

[a] Papermaking properties were determined on whole plant stem; seeds, leaves, and other plant parts were excluded.[4]
[b] M.E.A. = monoethanolamine procedure.
[c] Very little bast fiber.
[d] Gramineae have a single fiber type.

Table 9
POSSIBLE PRODUCTS AND YIELDS FROM MILKWEED (*ASCLEPIAS SYRIACA*) AS A POTENTIAL BOTANOCHEMICAL CROP

	Unimproved "wild" variety[a]		Developed new crop[b]		
Product	Percent of dry plant	Yield (kg/ha)	Percent of dry plant	Yield (kg/ha)	Potential uses
Natural rubber	1.6	197	4.0	897	Rubber-goods manufacture
Whole-plant (latex) oil	4.1	505	6.0	1,345	Chemical intermediates
Polyphenol fraction	7.2	888	10.0	2,242	Chemical intermediates
Seed — triglyceride oil	1.9	234	0.0	0	Edible oil
Seed — extracted meal	7.2	887	0.0	0	Foods and feeds (51% protein)
Extracted leaf — meal	16.0	1,973	33.0	7,397	Feeds (20% protein)
Floss	11.1	1,368	0.0	0	Insulating material
Bast fiber	11.0	1,356	6.0	1,345	Premium paper-making, cordage
Woody fiber — pod shells	12.3	1,517	0.0	0	Paper- and board-making, fuel, furfural
Woody fiber — stem shives	27.6	3,404	41.0	9,190	
Total	100.0	12,329	100.0	22,416	

[a] Based on dry weight and composition of a typical wild plant assuming a plant density of 107,635/ha.

[b] Assumes two cuttings per season with the plant not allowed to seed, combined genetic and agronomic improvement.

Table 10
OIL AND HYDROCARBON CROP MODELS, YIELD AND COMPOSITION[a]

	Rubber crop		Oil plus byproduct rubber crop		Oil crop		Gutta crop	
Component	Yield, kg/ha/year	Composition dry basis, %	Yield, kg/ha/year	Composition dry basis, %	Yield, kg/ha/year	Composition dry basis, %	Yield, kg/ha/year	Composition dry basis, %
Total dry matter	13,500	100	17,900	100	22,500	100	11,500	100
Crude protein	1,485	11	1,610	9	1,350	6	1,150	10
Rubber	1,350	10	360	2	—	—	—	—
Gutta	—	—	—	—	—	—	1,380	12
Oil	810	6	2,150	12	2,250	10	920	8
Polyphenol	945	7	1,250	7	4,050	18	805	7
Extracted residue[b]	10,395	77	14,140	79	16,200	72	8,395	73

[a] Yields are based on harvesting and using the entire aerial plant.
[b] Assuming little or no protein is extracted with the other components.

Table 11
LIPID CLASSES IN WHOLE-PLANT OILS, ESTIMATED BY THIN-LAYER CHROMATOGRAPHY

Plant source	Harvest date	Oil content (%)	Oil composition (%): Sterols	Other free alcohols	Free acids	Triglycerides	Non-glyceride esters	Hydrocarbons
Ambrosia trifida	9/20/77	4.21	11	4	7	68	7	3
Asclepias incarnata	7/28/77	2.70	9	15	8	13	48[a]	7
Asclepias syriaca	7/27/77	4.46	5	11	5	trace	72[a]	7
Cacalia atriplicifolia	8/3/77	2.99	10	24[b]	7	10	43	6
Campanula americana	9/8/77	6.51	13	5	10	58	10	4
Cirsium discolor	10/5/77	5.66	2	4	4	21	67[a]	2
Eupatorium altissima	9/20/77	6.08	6	5	7	36	44[a]	2
Euphorbia dentata	8/25/77	4.13	6	6	5	42	36[a]	5
Euphorbia lathyris	3/25/77	9.21	3	20	18	3[c]	49	7
Parthenium argentatum	5/13/77	4.04	10	7	5	23	31[a]	24
Rhus glabra	8/18/77	5.10	12	11	19	13	39	6
Sassafras albidum	9/8/77	2.26	8	46[b]	—	2	28	16
Sonchus arvensis	6/10/77	4.63	5	19	5	5	60[c]	6
Vernonia altissima	5/23/77	2.62	13	12	2	4	68[c]	1

[a] Prominent nonglyceride ester spot at RF ∿0.6 in addition to the one at RF ∿0.8.
[b] Prominent spot taken as free alcohol at RF ∿0.23.
[c] Small spot at RF ∿0.46 is unsaponifiable.

Table 12
IDENTIFICATION OF THE POLYMERIC HYDROCARBONS AND STEROLS IN LATICES FROM VARIOUS PLANT SPECIES[a]

Source	Rubber	Sterols	Sterols identified (in order of abundance)[a]
Asclepias sp. (Brazil)	3.5	31	a, b
Asclepias sp. (U.S.)	12	72	a, b
Euphorbia characias			g, c, j, i
E. coerulescens	1	75	d, e, m
E. lathyris	3	50	j, i, g, c, d
E. misera			d, c, i, m
E. obtusifolia			g, c, h, j, d
E. tirucalli	1	50	d, m, e
E. trigona	1.5	75	
Hevea brasiliensis	87	1	k, f, l
Manilkara zapota	14[b]	66	a, b

[a] Data shown are in percent of latex dry weight. The sterols were isolated from the latex by extraction with 10 volumes of acetone under reflux. After filtration, the acetone was evaporated and the residue was acetylated with a mixture of acetic anhydride and pyridine (4:1) at 60°C for 1 hr. The sterols were identified by gas-liquid chromatography and gas chromatography-mass spectrophotometry (GC-MS). The residue from the acetone extraction was then extracted with hot benzene to give the rubber fraction, which was analyzed by NMR. Abbreviations are as follows: a, α-amyrin acetate; b, β-amyrin acetate; c, cycloartenol; d, euphol; e, euphorbol; f, fucosterol; g, isomer of lanosterol; h, isomer of lanosterol; i, lanosterol; j, 24-methylene cycloartanol; k, β-sitosterol; l, stigmasterol; and m, tirucallol.

[b] 30% *Cis-* and 70% *trans-*polyisoprene (by NMR). Other samples were all *cis-*polyisoprene.

From Nielsen, P. E. et al., *Science*, 198, 942, 1977.

esters as extender oils and/or processing aids for rubber and as plasticizers for plastics. Some whole-plant oils are possibly directly useful in wax and polish formulations. A wide range of petrochemical products, as well as the whole range of tall oil, naval stores, and inedible fat products, is encompassed. The total market for such products is difficult to estimate but is very large. Moreover, if whole-plant oils can be produced at prices competitive with future petroleum prices, as seems possible, essentially unlimited markets exist as fuels and basic raw materials.[7]

Hydrocarbon Polymers

Most plants that produce hydrocarbon polymers contain natural rubber (NR), pure *cis-*1,4-polyisoprene. However, several of the Sapotaceae are traditional sources of gutta, *trans-*1,4-polyisoprene. Surprisingly, gutta has recently been found in four Gramineae species.

In general, north temperate zone plants have rubbers of much lower molecular weight than the *Hevea* rubber of commerce (Table 13). To be useful as a rubber polymer, a weight average molecular weight ($\overline{M}w$) above 2×10^5 is needed with a preferred value of 5×10^5 to 10^6. Lower $\overline{M}w$ rubbers would find lower value uses as plasticizers and processing aids for *Hevea* and synthetic rubbers, as liquid or easy-processing rub-

Table 13
MOLECULAR WEIGHT DISTRIBUTION OF THE RUBBER AND GUTTA FROM VARIOUS PLANT SPECIES[3]

Genus—species	Family	Common name	Molecular weight distribution: Weight average molecular weight, $\overline{M}w \times 10^{-3}$	Molecular weight distribution: Polydispersity, $\overline{M}w/\overline{M}n$
Potential rubber crops				
Parthenium argentatum	Compositae	Guayule	1280	6.1
Pycnanthemum incanum	Labiatae	Mountain mint	495	4.0
Lonicera tatarica	Caprifoliaceae	Red tatarian honeysuckle	298	3.8
Cacalia atriplicifolia	Compositae	Pale Indian-plantain	265	4.0
Solidago graminifolia	Compositae	Grass-leaved goldenrod	231	3.4
Solidago rigida	Compositae	Stiff goldenrod	164	3.1
Teucrium canadensis	Labiatae	American germander	130	3.8
Asclepias syriaca	Asclepiadiaceae	Common milkweed	120	3.1
Solidago leavenworthii	Compositae	Edison's goldenrod	118	2.2
Potential oil plus byproduct rubber crops				
Vernonia fasciculata	Compositae	Ironweed	417	3.7
Symphoricarpos orbiculatus	Caprifoliaceae	Coral berry	367	6.1
Silphium integrifolium	Compositae	Rosinweed	283	3.1
Cirsium discolor	Compositae	Field thistle	238	3.1
Silphium terebinthaceum	Compositae	Prairie dock	197	3.6
Campanula americana	Campanulaceae	Tall bellflower	113	2.4
Eupatorium altissimum	Compositae	Tall boneset	83	2.3
Ambrosia trifida	Compositae	Giant ragweed	72	1.9
Potential gutta crops				
Elymus canadensis	Gramineae	Canada wildrye	176	2.8
Phalaris canariensis	Gramineae	Canarygrass	123	3.5
Agropyron repens	Gramineae	Quackgrass	111	2.4

bers for special uses, and in adhesive formulation. Calvin suggests deliberate production of very low $\overline{M}w$ rubber as a feedstock for chemical intermediates and fuel production.[5] Rubber $\overline{M}w$ is probably genetically controlled; thus, plant breeding efforts might well be directed toward increasing both yield and $\overline{M}w$ in potential rubber crops and toward decreasing $\overline{M}w$ in oil plus by-product rubber crops. In the latter, there would be a processing savings associated with marketing low $\overline{M}w$ rubber as an unseparated oil component.

The $\overline{M}w$ of the new grass-gutta is low relative to most NR (Table 13). However, it is higher than that of the synthetic *trans*-polymer and adequate for most applications, since gutta has much greater crystallinity than NR.

Imported natural gutta has always been expensive and little used (Table 1). The synthetic polymer has mostly displaced the natural product in its largest present application, golf ball covers, but it is no longer manufactured in North America. However, gutta has a wide range of potential uses in competition with or supplementing established thermoplastics and thermosetting resins. Thus, a large market might be developed for gutta at a low price.

Polyphenols

There has long been an established market for polyphenols (tannins) in leather manufacture (Table 1). But this market is small compared to the potential production of soluble polyphenols from multiuse botanochemical crops.[3] Furthermore, the potential new products have not yet been well characterized.

Recently, there has been increased interest in low-cost polyphenols (bark extractives, for example) for wood-laminating resins, plywood glues, particleboard adhesives, fortifiers for starch adhesives, oil-well drilling muds, clay flocculants, plastics formulation, and antioxidants and in various specialty uses such as controlled-release (fertilizer) of iron and in herbicide formulations. Low-cost polyphenols can also be degraded to simple phenol intermediates.

Creosote bush (*Larrea tridentata*), a species not listed in any of the above tables, offers unique potential as an arid lands source of polyphenols for industrial uses. Its polyphenols have been well characterized[8] and proven to have utility in many of the above applications.[9] A lipophilic fraction of creosote bush resin provides antioxidant protection for guayule rubber produced in the Mexican pilot plant.[9] The proven effectiveness of the antioxidant both in this application and in vulcanized rubbers suggests that the product is ready for commercialization. The rubber antioxidant market alone would seem capable of supporting a botanochemical plant based on creosote bush as feedstock. Another proven, larger volume use for creosote bush resin products in adhesives makes these polyphenols especially attractive as potential new industrial materials.[9]

Polyphenols, like lower alcohols, are lower in calorific value than are whole-plant oils, hydrocarbons, or petroleum (Table 4). Thus, while an unlimited market exists for polyphenols as another source of basic chemicals and fuels, their value as a fuel is lower than that of petroleum.

Residues

A major product of botanochemical processing would be the extractive-free residue. Making the best use of this product presents a challenge, since its bulk requires either that it be consumed in the producing area or be processed to reduce bulkiness. Further, the value of the residue is critical to the economics of the system.

Maintenance of soil fertility normally requires return of plant residues in proportions depending on climate and cultural practices. Botanochemical processing would produce various nonconventional organic soil amendments even though none of the aerial plant might be directly returned to the soil. Examples of such optional soil amendments are animal manures, lignin from saccharification, sludge from methane production, and combustion ash. Such products should be compared and evaluated in the context of sustained botanochemical production. Botanochemical-producing crops capable of nitrogen fixing are highly desirable. An alternative might be companion cropping or crop rotation schemes.

Perhaps the highest use of the product would be to process, formulate, and pelletize it for sale as a supplemental cattle feed. The 8 to 14% actual protein content could be increased for cattle by ammoniating, adding urea, or even adding chicken manure. Total digestible matter could be increased by any of several treatments now being researched. Cattle would efficiently convert the semisynthetic feed to high-quality protein foods, valuable by-products, and a soil amendment. As a feed, the product's one disadvantage might be that fat-soluble vitamins had been removed. However, it could efficiently supplement conventional forages and, hopefully, could serve as a grain replacement.

Another scheme for residue utilization would be to classify it into high-protein leaf and low-protein stem fractions. Depending on crop species and agronomic variables, the leaf to whole-plant ratio varies from about 0.2 to 0.5, dry-weight basis. Dry leaf contains from about 1.5 to 1.9 times the protein content of whole-dry plant. Thus, a leaf meal of about 20% protein content could be separated by air classification or some other inexpensive process and marketed. The leaf meal would serve as a feed or perhaps even a food supplement. Part of the low-protein woody remainder could be burned on site for steam and power generation and the remainder briquetted and sold as a clean fuel.

A higher technology use for the residue, without losing its protein value, would be to saccharify it to provide a fermentation substrate. The main products would then be fuel alcohol, fodder yeast, acetone-butanol-ethanol, 2,3-butylene glycol, or any of several other products needed as fuels or raw materials. Xylose or furfural production could be integrated into the saccharification. Fermentation residues are generally high in protein and can go directly or indirectly as feeds into food production. The lignin by-product from saccharification is a good fuel and soil amendment. An ethanol yield of from 160 to over 200 L/metric ton of original residue would be reasonable.

There are many other good uses for extractive-free residue. Botanochemical processing could be integrated with production of paper-pulp by using organosolve pulping (Table 8). The residue could also be used for methane production or be pyrolyzed for charcoal and "wood distillation" products.

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